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CITATION:

Inada, Etsuko. The pressure and temperature effects on the Walden products of Na+, K+, Cs+ and I- in water. The Review of Physical Chemistry of Japan 1976, 46(1): 19-29

ISSUE DATE:

1976-06-30

URL:

http://hdl.handle.net/2433/47025

THE REVIEW OF PHYSICAL CHEMISTRY OF JAPAN, VOL. 46, NO. 1, 1976

THE PRESSURE AND TEMPERATURE EFFECTS ON THE WALDEN PRODUCTS OF Na^+, K^+, Cs^+ AND I^- IN WATER

BY ETSUKO INADA

The conductivities of NaI, KI and CsI in water were measured at 15, 25 and 40°C, up to 1500 kg/cm². The single ion limiting equivalent conductivities of Na^+, K^+, Cs^+ and I^- were calculated at each temperature and pressure. The interactions between these ions and solvent water molecules were deduced from their pressure and temperature coefficients of the Walden products. From the analysis of these quantities on the basis of Zwanzig's solvent relaxation theory, it was revealed that the present experimental results partly showed similar trends as the theory predicted. The discrepancies between the pressure coefficients of the Walden products calculated by this theory and the experimental values may be attributable to the incompleteness of the dielectric continuum model inherent to the theory. As regards I^-, it was found that the pressure coefficient of the Walden product was not so negative as was expected, in spite of its larger crystal radius compared with any alkali metal ion. This may be due to a difference in the orientation of water molecules around the cations and this anion.

Introduction

The effect of pressure on the conductivities of electrolytes in aqueous solution was first studied by Colladon and Sturm[1]. Since then a large number of papers on this effect have appeared. The important work to determine the limiting equivalent conductivity under high pressure was carried out in the 1950s by Hamann *et al.*[2,3] Unfortunately, the single-ion mobility which is indispensable for further understanding of the electrolyte solution was not determined by these authors. Only recently the transport numbers have been determined in detail at various pressures in our laboratory and others[4-7]. Therefore, by the aid of their results, we can obtain from the measurements of the conductivity the quantity which reflects the interactions between ions and solvent water molecules under high pressure. Recently, the conductivities of alkyl ammonium and monocarboxylate ions have been measured in our laboratory and their pressure dependences of the Walden products are interpreted in terms of the

(*Received December 4, 1975*)

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2) S. D. Hamann and W. Strauss, *Trans. Farady Soc.*, **51**, 1684 (1955)
3) J. Buchanan and S. D. Hamann, *ibid.*, **49**, 1425 (1953)
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density difference of water between in the hydration shell and in the bulk[8-11].

The main factors which significantly affect the mobilities of ions under high pressure are considered to be the compression effect[12,13], the pressure-induced desolvation[14,15], the electrostriction[16], the structural change of water[16] and the solvent relaxation effects[17,18]. In fact, it is difficult to say which effects are predominant in determining the ionic mobility under high pressure. However, the application of the theory of the solvent relaxation given by Zwanzig[19] to the ionic mobility under high pressure is very interesting, since there is no other appropriate formula expressing the ionic mobility at infinite dilution than that given by Zwanzig and since this theory gives one important step to a more quantitative theory. In addition, under high pressure there have been so far few cases dealt with by this theory. At atmospheric pressure, however, there have been many attempts to understand the interaction between ions and water molecules from this point of view[20-28]. In this paper, the interactions between ions and water molecules were studied at various pressures and temperatures, and the results obtained were interpreted in terms of Zwanzig's equation.

Experimental

NaI, KI and CsI were of the highest purity commercially available. All the salts were dried to a constant weight at *ca.* 100°C for 5 hrs. The concentration range in the conductivity measurements was *ca.* 0.001–0.01 N. The dilute sample solutions were prepared from the stock solutions (0.01 N) just in the same way as before[29]. The high-pressure apparatus and the conductivity cell were already described in the previous paper[29]. The measurements of the conductivities were carried out at 15, 25

8) M. Nakahara and J. Osugi, *This Journal*, **43**, 71 (1974)
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and 40°C and at the pressures up to 1500 kg/cm² (1 kg/cm² = 0.9807 × 10⁵ Pa).

Results

The conductivity theory of Fuoss and Onsager for nonassociated electrolytes in a dilute solution[30]

Table 1 $\Lambda'^{(P)}$ (ohm^{-1}·cm^2·equiv^{-1}) in watar

a. at 15°C

Salt / P(kg/cm²)	NaI	KI	CsI
1	102.3	122.2	125.6
200	103.1	122.9	126.3
400	103.3	123.5	126.5
600	103.3	123.8	126.4
800	103.2	123.7	126.0
1000	102.7	123.4	125.4
1200	102.2	122.8	124.6
1500	101.1	121.8	——

b. at 25°C

Salt / P(kg/cm²)	NaI	KI	CsI
1	127.2	150.6	154.6
200	127.5	150.6	155.0
400	127.3	150.7	154.8
600	127.0	150.4	154.2
800	126.3	149.8	153.1
1000	125.5	149.2	152.3
1200	124.6	148.3	151.1
1500	123.0	146.9	——

c. at 40°C

Salt / P(kg/cm²)	NaI	KI	CsI
1	168.6	196.9	201.1
200	168.4	197.0	200.3
400	167.3	196.1	198.9
600	166.5	195.2	197.6
800	165.2	194.1	195.8
1000	163.9	192.7	194.2
1200	162.5	191.2	192.3
1500	160.2	——	——

30) R. M. Fuoss and F. Accascina, "Electrolytic Conductance", Chap. 15, Interscience, New York (1959)

is applicable to the systems reported here. The limiting equivalent conductivity, $\Lambda^{\circ(P)}$, at pressure P can be determined from the following equation.

$$\Lambda = \Lambda^{\circ} - SC^{1/2} + EC\log C + JC. \qquad (1)$$

In eq. (1), C is the concentration; S and E are constants, which are functions of $\Lambda^{\circ(P)}$ and the solvent properties, viscosity and dielectric constant; J is a function of ion size taken as an adjustable parameter. The calculations of $\Lambda^{\circ(P)}$ were performed according to the method of Kay[31]. The calculated

Table 2 $\lambda^{\circ}\eta^{\circ}$ (ohm^{-1}·cm^2·equiv^{-1}·poise) in water

a. at 15°C

P (kg/cm^2) \ ion	Na^+	K^+	Cs^+	I^-
1	0.465	0.695	0.734	0.718
200	0.464	0.691	0.730	0.714
400	0.458	0.687	0.721	0.712
600	0.456	0.687	0.716	0.707
800	0.454	0.684	0.709	0.703
1000	0.450	0.682	0.705	0.701
1200	0.452	0.683	0.704	0.697
1500	0.451	0.686	——	0.693

b. at 25°C

P (kg/cm^2) \ ion	Na_+	K^-	Cs^+	I^-
1	0.448	0.657	0.693	0.689
200	0.448	0.654	0.693	0.685
400	0.445	0.653	0.689	0.684
600	0.445	0.653	0.686	0.680
800	0.442	0.651	0.680	0.678
1000	0.442	0.653	0.680	0.675
1200	0.441	0.653	0.678	0.673
1500	0.439	0.655	——	0.672

c. at 40°C

P (kg/cm^2) \ ion	Na^-	K^-	Cs^+	I^-
1	0.444	0.630	0.657	0.664
200	0.444	0.632	0.654	0.666
400	0.442	0.632	0.651	0.664
600	0.443	0.634	0.650	0.664
800	0.443	0.636	0.648	0.664
1000	0.443	0.638	0.648	0.663
1200	0.445	0.640	0.648	0.662

31) R. L. Kay, *J. Amer. Chem. Soc.*, 82, 2099 (1960)

values of $\Lambda^{\circ}(P)$ were shown in Table 1. The values of $\Lambda^{\circ}(P)$ of NaI and CsI have never been reported under high pressure. As regards KI, the relative Walden products, $\Lambda^{\circ}(P)\eta^{\circ}(P)/\Lambda^{\circ}(1)\eta^{\circ}(1)$, are nearly the same as those by Gancy and Brummer at 15 and 25°C[32], but a little higher at 40°C, where $\eta^{\circ}(P)$ is the viscosity of water at the pressure P, taken from the data by Cappi[33].

For each cation, the single-ion limiting equivalent conductivity, $\lambda^{\circ}(P)$, at the pressure P was calculated from the interpolated transport numbers of I^- in the aqueous solution of 0.02 N KI under high pressure[7], since it is shown that the pressure dependence of the transport numbers at 0.02 N are almost the same as those at infinite dilution[34]. The Walden products of each ion under the pressures, $\lambda^{\circ}(P)\eta^{\circ}(P)$, were calculated and the results are shown in Table 2. The relative Walden products, $\lambda^{\circ}(P)\eta^{\circ}(P)/\lambda^{\circ}(1)\eta^{\circ}(1)$, are plotted against pressure in Figs. 1, 2 and 3.

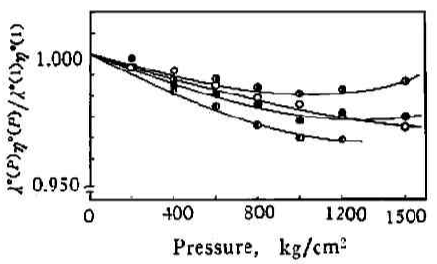

Fig. 1 Relative Walden products *vs.* pressure at 15°C
●: Na^+, ◑: K^+, ◐: Cs^+, ○: I^-.

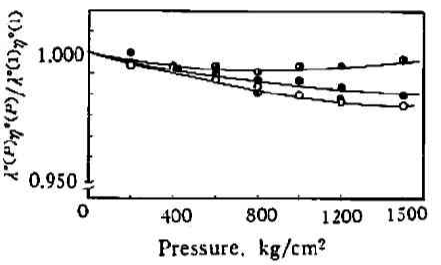

Fig. 2 Relative Walden products *vs.* pressure at 25°C
●: Na^+, ◑: K^+, ◐: Cs^+, ○: I^-.

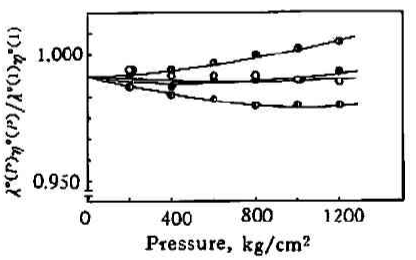

Fig. 3 Relative Walden products *vs.* pressure at 40°C
●: Na^+, ◑: K^+, ◐: Cs^+, ○: I^-.

From these figures the following features can be recognized.

1. The curves of the Walden products of Na^+, K^+ and Cs^+ tend at first to decrease and then to increase as the pressure increases.
2. The lower the temperature is, the deeper minima the curves have at higher pressure.
3. The pressure coefficients of the Walden products of Na^+, K^+ and Cs^+ decrease in the order of $K^+ > Na^+ > Cs^+$; this is different from the order expected from the magnitudes of their crystal radii.
4. As regards I^-, the pressure coefficients are not so small as those expected from the magnitude of

32) A. B. Gancy and S. B. Brummer, *J. Chem. Eng. Data*, **16**, 358 (1971)
33) J. B. Cappi, Ph. D. Thesis, London University (1964)
34) R. L. Kay, "Water," Vol. 3, Chap. 4, ed. by F. Frank, Prenum Press, New York-London (1973)

its crystal radius. The curves for I^- lie above those for Cs^+ (their crystal radii are 2.16 and 1.69 Å for I^- and Cs^+, respectively.).

These features can also be found in the data at 25°C by Kay[34].

Discussion

Pressure effects on the Walden products

When we analyse these results on the basis of the following Zwanzig equation[19],

$$\lambda^\circ\eta^\circ = Fe/(A_V\pi r + A_D\phi r^{-3}), \tag{2}$$

the pressure coefficient of the Walden product can be written as follows,

$$(\partial(\lambda^\circ\eta^\circ)/\partial P)_T = -Fe(\partial\phi/\partial P)_T A_D/\{r^2(A_V\pi r + A_D\phi r^{-3})^2\}. \tag{3}$$

In eq. (2), F and e are the Faraday constant and the protonic charge, respectively; r is the crystal radius of an ion; A_V and A_D are the proportional constants of the viscous and dielectric friction coefficients, respectively, and their numerical values will be given later, and

$$\phi = e^2(\varepsilon_0 - \varepsilon_\infty)\tau/\{\varepsilon_0(2\varepsilon_0 + 1)\eta\}, \tag{4}$$

where ε_0 and ε_∞ are the low- and infinite-frequency dielectric constants, respectively and τ is the solvent relaxation time. To derive eq. (3), only ϕ is taken to depend on pressure, and A_V and A_D are assumed to remain constant with pressure.

Since eq. (3) is a function of r, the right-hand side of eq. (3) can be represented by $f(r)$,

$$f(r) = (\partial(\lambda^\circ\eta^\circ)/\partial P)_T. \tag{5}$$

Then, the first derivative of $f(r)$ with respect to the radius r can be written as follows,

$$f'(r) = Fe(\partial\phi/\partial P)_T A_D r^{-3}(A_V\pi r + A_D\phi r^{-3})^{-3}(5A_V\pi - 3A_D\phi r^{-4}). \tag{6}$$

Equations (3) and (6) show that the pressure coefficient of the Walden product derived on the basis of the solvent relaxation theory is positive at any radius and has a maximum at $r_{max} = \{3A_D\phi/(5A_V\pi)\}^{1/4}$. The appearence of this maximum can qualitatively be interpreted in terms of the two opposite effects; one is the dielectric friction represented by the second term in the denominator of eq. (3), which is predominant at the smaller r, and the other is the viscous friction represented by the first term in the denominator of eq. (3), which is predominant at the larger r. Since there are no available data on the relaxation time τ at high pressure, the following theoretical equation on τ by Debye[35] was adopted in the calculation of ϕ.

$$\tau = 4\pi a^3\eta/kT, \tag{7}$$

where a is the radius of a water molecule. Taking it into account that $\varepsilon_0 \gg \varepsilon_\infty$ in the case of water, eq.

35) P. Debye, "Polar Molecule," p. 85, Dover Publications, INC., New York

(4) is approximated as

$$\phi \simeq 2\pi e^2 a^3 / kT\varepsilon_0 , \tag{8}$$

and then its first derivative with respect to pressure becomes,

$$(\partial\phi/\partial P)_T \simeq -\phi(\partial\varepsilon_0/\partial P)_T/\varepsilon_0 . \tag{9}$$

The theoretical curves, $(\partial(\lambda^\circ\eta^\circ)/\partial P)_T$ *vs.* r, can be obtained from eqs. (3), (8) and (9) in the two limiting cases[19],

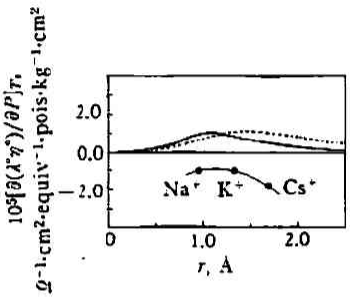

Fig. 4 Pressure coefficient of the Walden product *vs.* r at 15°C around 1 atm
——: theoretical curve in case A,
·····: theoretical curve in case B,
-●-: experimental result.
The theoretical curves have maxima in the region of $1.1<r<1.4$Å.

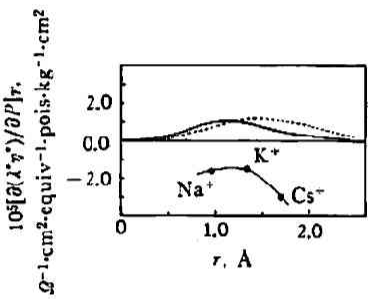

Fig. 5 Pressure coefficient of the Walden product *vs.* r at 25°C around 1 atm
——: theoretical curve in case A,
·····: theoretical curve in case B,
-●-: experimental result.
At this temperature the theoretical curves have maxima at r a little larger than that at 15°C, and lie below those at 15°C.

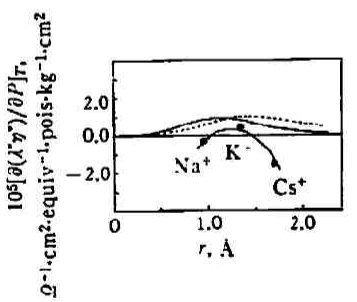

Fig. 6 Pressure coefficient of the Walden product *vs.* r at 40°C around 1 atm
——: theoretical curve in case A,
·····: theoretical curve in case B,
-●-: experimental result.
At this temperature the theoretical curves have maxima at r a little larger than those at 15 and 25°C and lie below those at 15 and 25°C.

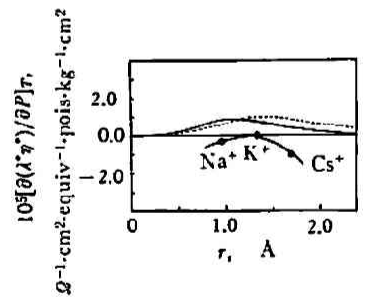

Fig. 7 Pressure coefficient of the Walden product *vs.* r at 15°C around 1000 kg/cm²
——: theoretical curve in case A,
·····: theoretical curve in case B,
-●-: experimental result.
At this pressure the theoretical curves have maxima at r a little smaller than that at 1 atm and lie below those at 1 atm.

$$\begin{aligned} &\text{A. perfect sticking:} \quad A_V=6\,, \quad A_D=3/8 \\ &\text{B. prefect slipping:} \quad A_V=4\,, \quad A_D=3/4 \end{aligned} \qquad (10)$$

They are shown in Figs. 4 to 7 together with the experimental results. The ionic radii are taken as 0.95, 1.33 and 1.69 Å for Na^+, K^+ and Cs^+, respectively[36]. The values of r_{max} calculated in both cases of A and B at 25°C around 1 atm are 1.1 and 1.4Å, respectively. Comparing the experimental results with the theoretical ones represented in Figs. 4 to 7, the following features are noted:

1. The theoretical curves lie in the positive region at any radius, while the experimental results have negative values as for the ions examined here.
2. The pressure coefficients of the Walden products are theoretically calculated to have maxima in the region of $1.1<r<1.4$ Å, and the experimental values decreases in the order of $K^+>Na^+>Cs^+$.
3. The pressure and temperature dependencies of the pressure coefficients of the Walden preducts derived from the theory are opposite to those obtained experimentally.

As regards the 1st feature, the fact that the so-called structure-breaking ions have excess mobilities in water at atmospheric pressure can explain their negative pressure coefficients of the Walden products[16], whose absolute values decrease with increasing pressure and temperature where there is found less extent of the structure of water. With respect to the 2nd feature, the sequence of the pressure coefficients of the Walden products of Na^+, K^- and Cs^+ in the experimental results show a similar tendency as the theory predicts; in both cases maxima exist in the neighbourhood of K^+ as shown in Figs. 4 to 7. Based on the two opposite effects mentioned just below eq. (6), it can theoretically be explained that K^+ has larger pressure coefficients of the Walden products than those of Na^+. This experimental fact has been discussed from a different stand-point of view[16,34].

As regards the 3rd finding, it is characteristic that in water the curve of the Walden product against pressure is concave upward up to *ca.* 2000 kg/cm^2, i. e., the pressure coefficient of the Walden product increases with increasing pressure. But above this pressure in water, and in other solvents, the curves of the Walden products are always concave downward against pressure[8,15,17,18,34]. Under these conditions where the solvents are more normal liquids, the theory seems to work well in knowing the pressure dependency of the pressure coefficient of the Walden product. In the present study, the discrepancies between the experimental results and the theoretical curves become smaller at the higher pressure and temperature. in other words, the experimental results approach more closely to the theoretical ones with increasing pressure and temperature. So, these discrepancies which are more distinctive at the lower pressures and temperatures might be attributed to the incompleteness of the dielectric continuum model or structure neglection inherent to the theory. However, it is yet uncertain whether or not our present explanations on the behavior of the ions in water are reasonable before we see how the Walden products vary against pressure at much higher pressures.

Upon examining the experimental values on the alkali ions (Li^+, Na^+, K^+) in methanol at 25°C reported by Kay[34], the following facts can be noted:

36) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," p. 461, Butterworths Scientific Publications, London (1965)

1. The pressure coefficients of the Walden products are positive.
2. They decrease in the order of $K^+ > Li^+ \gtrsim Na^+$.
3. They decrease with increasing pressure.
4. They have much larger values than those in water.

The 1st and 3rd are explained by Zwanzig's theory, and the 2nd is not completely but more successfully explained for Li^+ in methanol than that in water. But the 4th can not be explained, because, due to the much larger value of ϕ in methanol[34], the theoretical curve for the pressure coefficient of the Walden product lies lower than that of water in the region of at least $r<2$ Å.

Anyhow, the data on many ions in various kinds of non-aqueous solvents will be needed to confirm whether Zwanzig's equation works well.

Temperature effects on the Walden products

In a similar manner as described in the previous section, the following equations are derived,

$$(\partial(\lambda^\circ\eta^\circ)/\partial T)_P = -Fe(\partial\phi/\partial T)_P A_D/\{r^2(A_V\pi r + A_D\phi r^{-3})^2\}, \tag{11}$$

$$g(r)=(\partial(\lambda^\circ\eta^\circ)/\partial T)_P, \tag{12}$$

$$g'(r)=Fe(\partial\phi/\partial T)_P A_D r^{-3}(A_V\pi r + A_D\phi r^{-3})^{-2}(5A_V\pi - 3A_D\phi r^{-4}), \tag{13}$$

and

$$(\partial\phi/\partial T)_P \simeq -\phi(1/T + (\partial\varepsilon_s/\partial T)_P/\varepsilon_s). \tag{14}$$

As easily seen from eq. (13), the theoretical curves, $(\partial(\lambda^\circ\eta^\circ)/\partial T)_P$ *vs.* r, have minima at r_{min}, the same radius where the pressure coefficients of the Walden products take maxima. The curves obtained are shown in Figs. 8 and 9 together with the experimental results. The data from Ref. 34 are also shown

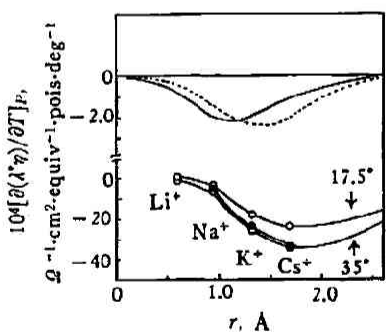

Fig. 8 Temperature coefficieat of the Walden product *vs.* r at 25°C around 1 atm
——: theoretical curve in case A,
·····: theoretical curve in case B,
-●-: experimental result,
-○-: recalculated from the graphical data of Ref. 34.
The theoretical curves have minima in the region of $1.1<r<1.4$ Å.

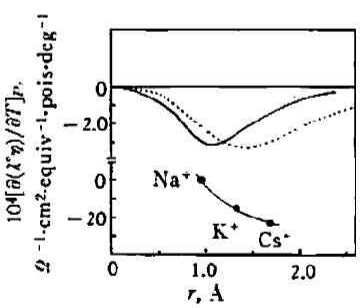

Fig. 9 Temperature coefficient of the Walden product *vs.* r at 25°C around 1000 kg/cm²
——: theoretical curve in case A,
·····: theoretical curve in case B,
-●-: experimental result.
At this pressure the theoretical curves have minima at r a little smaller than those at 1 atm and lie below those at 1 atm.

in Fig. 8.

Comparing the experimental results with the theoretical ones, the following features are noted:

1. The variation in the temperature coefficients of the Walden products against the crystal radius of an ion agrees well with the theoretical ones so far as $r<r_{min}$, and both experimental data by Kay[34] and the theoretical curves have minima against r; this is different from the considerations by the other authors[23].
2. The pressure dependencies of the temperature coefficients of the Walden products expected from the theory are opposite to those obtained experimentally (however, the experimental results approach more closely to the theoretical ones with increasing pressure.).

Pressure dependence of the Walden product of I^-

Because of lack of the data on the halide ions in our present study, the curves for the pressure coefficients of the Walden product against their crystal radii can not be drawn. But from the approximate calculations of the pressure coefficients of the Walden products for F^-, Cl^-, Br^-[34] and I^- at 25°C, it is found that they decrease monotonously in the order of $F^->Cl^->Br^->I^-$ against their crystal radii; this tendency is expected from the solvent relaxation theory at $r>r_{max}$. Another important feature is that the experimental curves for the halide ions lie above those for the alkali metal ions. This fact may be attributed to the difference in the orientation of water molecules around the cations and the anions.

It is a long-standing problem how water molecules orient around halide ions and many discussions have been made about it[6,37-40]. Two types of orientations are proposed which are shown in Fig. 10.

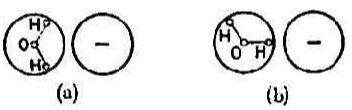

Fig. 10 Two types of the orientation of a water molecule in the vicinity of an ion

In the case of Cl^-, the water molecules are expected to orient in type (b), in view of the pressure dependence of the Walden products[41]. Herz has concluded from the NMR studies that the orientation around F^- is type (b), while that around I^- is type (a)[40]. Judging from our experimental results for I^-, the orientation of water molecules around I^- seems to be type (b) which would add a positive value to the pressure coefficient of the Walden products. Consequently, in spite of the large size of the crystal radius, the pressure coefficients of the Walden products are not so much negative.

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Acknowledgement

The author is grateful to Prof. Jiro Osugi for his continued interest and valuable suggestions.

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